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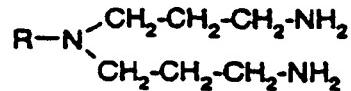
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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WO 01/21679 A1

(54) Title: ALKYLDIPROPYLENENTRIAMINES AND THEIR ADDUCTS AS HARDENERS FOR EPOXY RESINS



(1)

(57) Abstract: A curable composition comprising a) an epoxy resin having on average more than one epoxide group per molecule and b1) an alkyldipropyleneetriamine of general formula (I) and/or b2) an adduct of an alkyldipropyleneetriamine of general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule in which R is a hydrocarbon radical having 8 to 22 carbon atoms, and the use of this composition for coating mineral and metallic substrates.

Alkyldipropylenetriamines and their adducts as hardeners for epoxy resins

The present invention relates to alkyldipropylenetriamines and their adducts with epoxide compounds having on average at least one epoxide group per molecule as hardeners for epoxy resins and to the use of curable compositions based on these alkyldipropylenetriamines and adducts and epoxy resins for coating mineral and metallic substrates.

Curable compositions based on amine curing agents and epoxy resins are widely used in industry to coat and enhance metallic and mineral substrates. Amine curing agents used in particular are aliphatic, cycloaliphatic or aromatic amines and also polyaminoamides with or without imidazoline groups.

The mechanical and physical properties of the curable compositions based on these amines are adequate for numerous applications.

Especially for the coatings sector, however, there is a requirement for binder systems which are surface tolerant, i.e., which exhibit good adhesion even on substrates that are difficult to coat, such as moist substrates or unpretreated metal panels, for example, and which ensure the very best protection of the substrate, e.g. corrosion protection. There is also a requirement for rapid initial curing of the binder systems following application to the substrates, even at low temperatures, in order, for example, to ensure that the substrates can soon withstand loading or be coated further.

High early water resistance of the still uncured film (for example, by forming droplets at high relative atmospheric humidities) is an important criterion, as is a low viscosity of the binder, so that it can still be processed even at low temperatures.

Known hardeners for epoxy resins which afford relatively good corrosion protection and exhibit serviceable adhesion even on difficult substrates include polyaminoamides, which normally contain imidazoline groups. These compounds are prepared by condensing generally unsaturated, long-chain fatty acids with polyethylenepolyamines. The disadvantage of these compounds is their high viscosity at low temperatures (< 15°C) and also the slow

rate of initial cure and/or through-cure. Moreover, compounds of this type possess relatively high colour numbers.

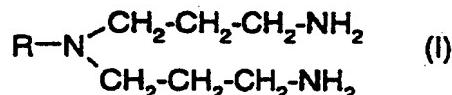
It was therefore an object of the present invention to eliminate these disadvantages.

This object is achieved through the use of the curable compositions of the invention, comprising alkylidipropylenetriamines and/or their adducts with epoxide compounds which contain on average at least one epoxide group per molecule with epoxy resins.

It has surprisingly been found that the alkylidipropylenetriamines and/or their adducts of the invention, although similar in structure to the polyaminoamides with or without imidazoline groups, possess a much higher rate of initial cure and/or through-cure, especially at low temperatures of < 15°C. Moreover, these compounds have, in comparison, a much lower viscosity and colour number.

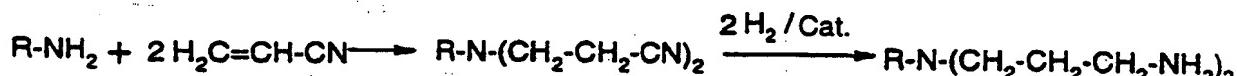
The invention provides curable compositions comprising

- a) an epoxy resin having on average more than one epoxide group per molecule and
- b1) an alkylidipropylenetriamine of the general formula (I) and/or
- b2) an adduct of an alkylidipropylenetriamine of the general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule



in which R is a hydrocarbon radical having 8 to 22, preferably 10 to 20, carbon atoms.

The compounds of the formula (I) are normally prepared by cyanoethylation of amines (fatty amines) and subsequent hydrogenation in accordance with conventional methods. The amines or, respectively, fatty amines are reacted with acrylonitrile, and then the cyanide groups are hydrogenated in the presence of a catalyst. Schematically, the reaction sequence is as follows:



The fatty amines used preferably as reactants for the cyanoethylation are mixtures of long-chain primary alkylamines, obtained from mixed glycerol esters of medium and higher fatty acids with an even number of carbons, as occur in plant or animal bodies. For example,

bovine tallow contains almost 100% (esterified) fatty acids having a carbon chain length of 14, 16 and 18 carbon atoms. The bovine tallow fatty amines obtained from bovine tallow are available commercially as tallow fatty amine, for example as Genamin® TA100 (Clariant). Therefore, if adducts of the invention are prepared starting from fatty amines of natural products, the products of the general formula (I) comprise mixtures of compounds with different chain lengths R. The chains R have approximately 8 to 20 carbon atoms, not more than approximately 22 carbon atoms, and may either be saturated or contain multiple bonds and may be either straight-chain or branched. Further examples of commercially available fatty amines which may be used in accordance with the invention, besides tallow fatty amine, are saturated straight-chain fatty amines such as dodecylamine, tetradecylamine, for example, saturated, branched fatty amines such as isotridecylamine, for example, unsaturated and saturated fatty amines and fatty amine mixtures, such as coconut fatty amine, oleylamine, rapeseed oil fatty amine, for example, or else stearylamine.

The present invention provides b2) adducts of compounds of the formula (I) with epoxide compounds containing on average at least one epoxide group per mole (b3). The adducts of the invention are prepared by known methods, by adding the epoxide compounds dropwise at 50°C - 100°C with stirring to the initial charge of alkylidipropylenetriamine and then stirring the mixture at the same temperature for about 30 minutes until formation of adducts is at an end.

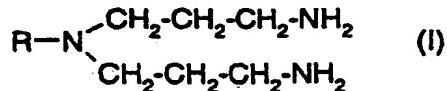
Also used are what are known as "isolated adducts", which are prepared with an excess of alkylidipropylenetriamine. In this case, from 1.5 to 10, preferably 4-6, times the molar amount of amine are introduced as the initial charge and the epoxide compound is added dropwise with stirring, judiciously at 50-100°C. Subsequently, the excess amine is removed by distillation under reduced pressure.

The invention further provides a process for preparing the adduct, which comprises heating an alkylidipropylenetriamine of the formula (I) to reaction temperature (50-100°C), subsequently adding at least one epoxide compound (F) having on average at least one epoxide group in the molecule, with continued stirring, and finally, after the formation of adducts has ended, removing any excess alkylidipropylenetriamine from the reaction mixture.

In accordance with the invention, both the compounds of the formula (I) and the adducts with epoxide compounds that have derived from the compounds of the general formula (I) may be used as hardeners for epoxide compounds. Similarly, mixtures comprising at least one compound of the formula I and at least one adduct of compounds of the formula I with epoxide compounds may be used as hardeners for epoxide compounds. Similarly, mixtures of compounds of the formula (I) or, respectively, their adducts may be used in which the compounds of the formula (I) may have hydrocarbon radicals R which are different in terms of the respective chain length (8 to 20 carbon atoms), degree of branching and bond order. Moreover, the curable compositions of the invention may comprise further amine curing agents, with or without the use of solvents, plasticizers, UV stabilizers, dyes, pigments and fillers.

The invention therefore additionally provides curable compositions comprising

- a) an epoxy resin having on average more than one epoxide group per molecule and
- b1) an alkylidipropylenetriamine of the general formula (I) and/or
- b2) an adduct of an alkylidipropylenetriamine of the general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule



in which R is a hydrocarbon radical having 8 to 22, preferably 10 to 20, carbon atoms, and, if desired, further optional components selected from

- c) diluents, other amine components and other customary auxiliaries and additives.

The modifiers c) may be added equally to the hardener b) of the invention, to the resin a), with the exception of the amine component, or to the curable composition.

The curable compositions of the invention, comprising compounds of the general formula (I) and their adducts, are preferably adjusted with the modifiers to a preferred mixing ratio of 50-100 parts by weight of hardener per 100 g of epoxy resin (a). Depending on the establishment of desired end properties, the mixing ratios may also be below 50 and, respectively, above 100 parts by weight of hardener per 100 g of resin (a).

The fraction of diluents should not exceed 40%, based on the hardener, since otherwise there is too great a drop in the mechanical data.

The ratio of reactive groups of the compounds of the general formula (I) and their adducts and any additional amines to the epoxide groups (a) and, if present, the epoxide compounds as per (b3) is preferably established at equivalence. Here too, however, depending on the establishment of desired properties, there may be deviations, in some cases very sharp, from equivalence, including both upward and downward deviations. The fraction of the hardeners of formula I and/or their adducts in the curing agent is between 10 and 70%, preferably between 20 and 50%.

As diluents it is possible to use both compounds which largely remain in the thermoset after curing, such as high-boiling alcohols and ethers such as benzyl alcohol, ethylene glycol, propylene glycol, butyl diglycol, etc., and compounds which predominantly evaporate from the coating in the course of curing, such as xylene, butanol, methoxypropanol, and also water, for example.

As additional amine components and for establishing the end properties it is possible to use all customary amines, such as polyethylene polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, etc.; polypropylenopolyamines such as dipropylenetriamine, tripropylenetetramine, and also the polyamines obtained by cyanoethylation of polyamines, especially of ethylenediamine, and subsequent complete or partial hydrogenation; aliphatic amines such as diaminoethane, diaminopropane, neopentanediamine, diaminobutane, hexamethylenediamine, 2,2,4(2,4,4)-trimethyl-1,6-hexamethylenediamine; cycloaliphatic polyamines such as isophoronediamine, diaminocyclohexane, norbornanediamine, 3(4),8(9)-bis(aminomethyl)tricyclo[5.2.1.0]decane (TCD-diamine), 1,3-bis(aminomethyl)cyclohexane, bis(aminomethylcyclohexyl)methane; heterocyclic polyamines such as N-aminoethylpiperazine, 1,4-bis(aminopropyl)piperazine; araliphatic amines such as xylylenediamine; polyoxyalkylenepolyamines; aromatic amines, such as diaminodiphenylmethane, for example; polyaminoamides with or without imidazoline groups, such as condensation products of monomeric or dimeric fatty acids with polyethylenepolyamines, for example.

The epoxide compounds (b3) used for forming adducts with the aforementioned alkylidipropylenetriamines are the known and commercially customary products having at least one epoxide group per molecule. Preference is given in accordance with the invention

to glycidyl ethers based on monohydric or polyhydric phenols, such as phenol, cresol, bisphenol A, bisphenol F, novolaks, monohydric or polyhydric aliphatic alcohols having 4 to 18 carbon atoms, such as butanol, butanediol, hexanol, hexanediol, fatty alcohols having a chain length of 8 to 18 carbon atoms, polyoxyalkylene glycols such as diethylene glycol, dipropylene glycol, polyoxypropylene glycol, polyoxyethylene glycols, diethylene glycol monobutyl ether, and also epoxide compounds prepared by direct epoxidation, such as styrene oxide. As epoxide compound (b3) preference is given in particular to bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, cresyl glycidyl ether and fatty alcohol glycidyl ethers.

The degree of adduct formation may be varied within wide limits and is influenced by the nature of the amine compound and by the nature of the epoxide compound, and may also be tailored to the respective field in which the curable composition is employed.

Positive results are generally always obtained using from 0.1 to 1 mol of the epoxide compound per mole of the amine compound, so that on average there are more than 2 free amine hydrogens in the adduct.

The epoxide compounds (a) used in accordance with the invention are commercially customary products having on average more than one epoxide group per molecule, and are derived from monohydric and/or polyhydric and/or polycyclic phenols, especially bisphenols, and also novolaks, for example, bisphenol A diglycidyl ether and bisphenol F diglycidyl ether. An extensive listing of these epoxide compounds may be found in the handbook "Epoxidverbindungen und Epoxidharze" [Epoxide Compounds and Epoxy Resins] by A.M. Paquin, Springer Verlag, Berlin, 1958, Chapter IV, and in Lee & Neville, "Handbook of Epoxy Resins", 1967, Chapter 2. It is also possible to use mixtures of two or more epoxide compounds (a). Preference is given in accordance with the invention to mixtures of glycidyl ethers based on bisphenol A, bisphenol F or novolaks with what are known as reactive diluents, such as monoglycidyl ethers of phenols or glycidyl ethers based on monohydric or polyhydric aliphatic or cycloaliphatic alcohols, for example. Examples of such reactive diluents are phenyl glycidyl ether, cresyl glycidyl ether, p-tert-butylphenyl glycidyl ether, butyl glycidyl ether, C12-C14 alcohol glycidyl ethers, butane diglycidyl ethers, hexane diglycidyl ethers, cyclohexanedimethyl diglycidyl ethers or glycidyl ethers based on polyethylene glycols or polypropylene glycols. If necessary, the viscosity of the epoxy resins may be

reduced further by adding these reactive diluents. As the epoxide compound (a), particular preference is given to bisphenol A diglycidyl ether and bisphenol F diglycidyl ether.

The customary auxiliaries and additives may also be admixed to the curable compositions of the invention, examples being fillers such as gravels, sands, silicates, graphite, silica, talc, mica, etc., in the particle size distributions customary in this field, and also pigments, dyes, stabilizers, levelling/plasticizing agents, non-reactive extender resins and plasticizers.

On the basis of their advantageous properties, the curable compositions of the invention are suitable for processes for coating mineral (e.g. concrete, screeding) and metallic substrates, especially where the substrates to be coated are difficult. Difficult-to-coat substrates are, for example, moist substrates, in the form, for example, of fresh concrete floors, and also substrates with little, no or poor pretreatment. In these cases the curable compositions of the invention are found, surprisingly, to be highly surface tolerant, in the sense that they generally lead to good adhesion of the coating even to non-pretreated substrates. On the basis of the rapid initial cure and through-cure, and high early water resistance, that is achievable, and on the basis of their comparatively low viscosity, therefore, the compositions of the invention also enable coatings to be applied and through-cured under difficult external conditions, by which are meant relatively low temperatures of below 30°C down into the freezing point range, and relatively high atmospheric humidities of 50% to 100%.

Coating may take place by conventional techniques, by applying the curable composition from the liquid, slurry or pastelike state by brushing, spreading, painting, dispersion-coating or melt-coating, by extrusion, flow coating or dipping, or as a so-called hot-melt. The components of the curable composition are not combined and substantially homogenized until a short time before their use. After coating has taken place, the compositions of the invention may be cured by heating at moderately elevated (30-100°C) temperatures. The curing time is, of course, dependent on the respective application conditions, such as coating thickness, substrate properties, external conditions, etc. A key advantage in accordance with the invention, however, is that rapid initial cure and substantial through-cure of the coatings is possible without external supply of heat on the sole basis of the prevailing external ambient temperatures, which may be between 0 to 5°C and 30°C, and in particular below 15°C.

The invention therefore further provides, in addition, the cured compositions of the invention.

#### Analytical methods

##### Viscosity

Measured with a Haake RV 20 rotational viscometer in accordance with the manufacturer's instructions.

##### Colour number

Measured in accordance with DIN 53 995 using the Lovibond colorimeter (Gardner colour number, APHA colour number).

##### Amine number

Measured in accordance with DIN 16 945.

##### Tecam value

Value for the gel time measured with the Tecam gelation timer GT3 from Techne, Cambridge, GB, at 23°C and 50% relative atmospheric humidity.

Sample mixture of resin and hardener and accelerator = 250 g.

##### Shore D hardness

Measured with the instrument type 38009 from Karl Frank GmbH on test specimens of 30 mm in diameter and 6 mm in thickness after 1 day and 7 days and after 2 days and 24 hours of storage at 70°C.

##### Early water resistance/blushing of the film on water exposure

###### Sample preparation:

The calculated amounts of epoxy resin and amine hardener are weighed out into the mixing vessel and mixed thoroughly for approximately 2 minutes using a spatula without incorporating air to an excessive extent. Local inhomogeneities show up as smearing and are to be avoided.

A 500 µm film-drawing frame from Erichsen is placed on a glass plate which has been cleaned with acetone and then dried, and the frame is filled with approximately 15 g of the reactive mixture and drawn uniformly over the free area. The freshly coated glass plates are

immediately placed in the corresponding controlled-climate chambers, typically at a relative atmospheric humidity (RH) at 23°C of approximately 95%, at 10°C of approximately 80%.

To determine the early water resistance, the glass plates are brought back into the testing laboratory after 24 h of curing.

For the test, evaluation figures (along the lines of DIN 53230) are awarded:

- 0 = no defect
- up to 5 = very severe defects.

In the case of precision differentiation, using comparison samples, for example, gradations of 0.5 are possible.

Approximately 0.5 ml of fully deionized water is applied by pipette to an area of each plate, and is dabbed off with cellulose after 60 minutes.

An assessment is made of the extent of coloration/blushing of the film at the water-exposed area.

#### Examples

##### Example 1 (Hardener)

N,N-Bis-amino-propyl-tallow fatty amine, prepared by reacting tallow fatty amine (a mixture of saturated and unsaturated alkylamines having 14-20 carbon atoms) with acrylonitrile and then hydrogenating the cyanide groups.

##### Example 2 (Hardener + diluent)

90 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and 10 g of benzyl alcohol are homogenized at room temperature.

##### Example 3 (Adduct + diluent)

80 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and 10 g of benzyl alcohol are introduced into a reaction vessel, then 10 g of a bisphenol A diglycidyl ether having an epoxide equivalent weight of 185 are added continuously over the course of approximately 20 minutes at 60-90°C.

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Stirring is continued for about 10 minutes and then the mixture is cooled to room temperature.

Example 4 (Adduct + diluent)

The following are reacted in accordance with Example 3:

80 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and  
10 g of cresyl glycidyl ether (epoxide equivalent approximately 180), and also  
10 g of benzyl alcohol.

Example 5 (Adduct + diluent)

The following are reacted in accordance with Example 3:

90 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1 and  
10 g of a long-chain aliphatic glycidyl ether having an epoxide equivalent weight of 315, and  
10 g of benzyl alcohol.

Example 6 (Hardener + amine co-hardener + diluent)

40 g of N,N-bis-amino-propyl-tallow fatty amine as per Example 1,  
27 g of isophoronediamine and  
33 g of benzyl alcohol  
are homogenized at room temperature.

Example 7 (Adduct + diluent)

The following are reacted in accordance with Example 3:

50 g of lauryldipropylenetriamine (prepared as per Example 1 on the basis of laurylamine (alkylamine mixture having 8-18 carbon atoms per molecule)) and  
20 g of a commercially customary glycidyl ether based on bisphenol A, having an epoxide equivalent weight of 185 g/eq, and  
30 g of benzyl alcohol  
are homogenized at room temperature.

Example 8 (Comparative hardener)

Standard commercial polyaminoimidazoline, prepared by condensing triethylenetetramine and tall oil fatty acid by conventional techniques.

Example 9 (Comparative adduct + diluent)

80 g of the polyaminoimidazoline as per Example 8 and 10 g of benzyl alcohol are introduced into a reaction vessel, then 10 g of a bisphenol A diglycidyl ether having an equivalent weight of 185 are added continuously over the course of approximately 20 minutes at 60-90°C.

The mixture obtained is subsequently stirred for 10 minutes and then cooled to room temperature.

Example 10 (Comparative hardener)

Standard commercial polyaminoimidazoline, prepared by condensing triethylenetetramine and dimerized talloil fatty acid by a conventional technique.

The properties and measurements obtained for Examples 1-10 are listed in Table 1.

**Table 1**

Example/ Measurements	1	2	3	4	5	6	7	8	9	10
Viscosity in mPa.s/25°C	26	33	141	40	35	24	195	250	1720	16000
Amine number mg KOH/g	430	385	345	385	385	350	275	390	312	390
Colour number (Gardner)	<1	1	1-2	1-2	1	<1	<1	8	7	8
g hardener per 100 g resin <sup>1</sup>	50	55	60	60	60	50	100	50	60	50
Tecam value (min)	175	103	102	135	168	76	85	180	205	120

Shore D hardness development at 10°C:

1 Day	21	28	11	10	5	43	54	0	0	11
2 Days	52	63	49	45	37	68	72	37	20	49
Final hardness <sup>2</sup>	77	76	78	76	74	80	80	78	77	75

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**Early water resistance after 24-hour storage at:**

10°C/80% RH	0.5	0	0	0	1	2	1-2	3	4	3
23°C/50% RH	0	0	0	0	0	0	0	1	3	2

**Notes:**

RH = relative atmospheric humidity

- <sup>1)</sup> Araldite GY 250 = commercial epoxy resin based on bisphenol A, epoxide equivalent weight: 185
- <sup>2)</sup> Curing for 2 days at room temperature and 24 hours at 70°C

## WHAT IS CLAIMED IS:

- Schätz 7*
1. A curable composition comprising
    - a) an epoxy resin having on average more than one epoxide group per molecule and
      - b1) an alkyldipropylenetriamine of the general formula (I) and/or
      - b2) an adduct of an alkyldipropylenetriamine of the general formula (I) with b3) an epoxide compound having on average at least one epoxide group per molecule

$$\begin{array}{c} \text{R}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \end{array} \quad (\text{I})$$

in which R is a hydrocarbon radical having 8 to 22, preferably 10 to 20, carbon atoms.

  2. A curable composition according to claim 1, further comprising c) diluents and/or other amine components and/or other customary auxiliaries and additives.
  3. A curable composition according to either claim 1 or claim 2, wherein the composition is derived from compounds of the formula (I) with different hydrocarbon radicals R.
  4. A curable composition according to any one of claims 1 to 3, wherein component a) is a bisphenol A diglycidyl ether or bisphenol F diglycidyl ether.
  5. A curable composition according to any one of claims 1 to 4, wherein component b) is a bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, cresyl glycidyl ether or fatty alcohol glycidyl ether.
  6. A cured composition comprising a composition according to any one of claims 1 to 5.
  7. The use of a composition according to any one of claims 1 to 5 for coating mineral and metallic substrates.
- Add A27*

## PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION  
(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

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in its capacity as elected Office

Date of mailing (day/month/year) 22 May 2001 (22.05.01)	
International application No. PCT/EP00/08970	Applicant's or agent's file reference CS/K-22077/PCT/A/CSB
International filing date (day/month/year) 14 September 2000 (14.09.00)	Priority date (day/month/year) 23 September 1999 (23.09.99)
<b>Applicant</b> <b>SCHERZER, Wolfgang et al</b>	

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

29 March 2001 (29.03.01)

in a notice effecting later election filed with the International Bureau on:

\_\_\_\_\_

2. The election  was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Olivia TEFY
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## PATENT COOPERATION TREATY

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REC'D 27 SEP 2001  
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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference CS/K-22077/PCT/A/CSB	<b>FOR FURTHER ACTION</b>		See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP00/08970	International filing date (day/month/year) 14/09/2000	Priority date (day/month/year) 23/09/1999	
International Patent Classification (IPC) or national classification and IPC C08G59/50			
<p><b>Applicant</b> VANTICO GMBH &amp; CO. KG et al.</p>			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I    <input checked="" type="checkbox"/> Basis of the report</li> <li>II    <input type="checkbox"/> Priority</li> <li>III    <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV    <input type="checkbox"/> Lack of unity of invention</li> <li>V    <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI    <input type="checkbox"/> Certain documents cited</li> <li>VII    <input type="checkbox"/> Certain defects in the international application</li> <li>VIII    <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>			

Date of submission of the demand 29/03/2001	Date of completion of this report 25.09.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Rousseau, F  Telephone No. +49 89 2399 8297



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/08970

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):  
**Description, pages:**

1-12 as originally filed

### Claims, No.:

1-7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
  - the language of publication of the international application (under Rule 48.3(b)).
  - the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description,        pages:
- the claims,           Nos.:
- the drawings,        sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP00/08970

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:      Claims 5
	No:      Claims 1-4,6,7
Inventive step (IS)	Yes:      Claims
	No:      Claims 5
Industrial applicability (IA)	Yes:      Claims 1-7
	No:      Claims

2. Citations and explanations  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP00/08970

1. The subject-matter of present claims 1 to 4, 6 and 7 is anticipated by US-A-3 280 074 (D1) (see claims 1, 5 and passages column 7, lines 4-55 and column 8, lines 24-44). Hence, the subject-matter of present claims 1 to 4, 6 and 7 does not meet the requirements of Art. 33(2) PCT.
2. The subject-matter of present claim 5 differs from D1 in that the curing agent is an adduct b2) as defined in present claims 1 to 5 instead of b1). In view of the results summarized in table 1, page 11 of the present description, the objective technical problem solved by the use of b2) instead of b1) can be seen as to provide further epoxy resin composition suitable for coatings. The use of epoxide adducts of known polyamine curing agents instead of the polyamine curing agent as such is well known in the field of epoxy resin coating compositions (see US-A-4 195 152 (D2), claim 1, example 6, column 4, lines 40-43, US-A-4 310 695 (D3), claims 1-5, column 5, lines 14-19 and JP-A-10-140 125 (D4)). Thus, if a skilled person starting from D1 wanted to provide further epoxy resin compositions suitable for coatings, it would have been obvious for him in view of D2, D3 and D4 to try as curing agent the adduct b2) instead of b1).
3. The subject-matter of claims 1 to 7 is industrially applicable.
4. In claim 5, "component b)" should read "component b3)" (Art. 6 PCT).

## PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

**NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES**

(PCT Rule 47.1(c), first sentence)

<b>Date of mailing (day/month/year)</b> 29 March 2001 (29.03.01)			
<b>Applicant's or agent's file reference</b> CS/K-22077/PCT/A/CSB		<b>IMPORTANT NOTICE</b>	
<b>International application No.</b> PCT/EP00/08970	<b>International filing date (day/month/year)</b> 14 September 2000 (14.09.00)	<b>Priority date (day/month/year)</b> 23 September 1999 (23.09.99)	
<b>Applicant</b> VANTICO GMBH & CO. KG et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
**AU,KR,US**

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
**BR,CA,CN,EP,HU,JP,MX,PL,RU,TR**

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 29 March 2001 (29.03.01) under No. WO 01/21679

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland	<b>Authorized officer</b>  <b>J. Zahra</b>
<b>Facsimile No. (41-22) 740.14.35</b>	<b>Telephone No. (41-22) 338.83.38</b>

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>CS/K-22077/PCT/A/CSB</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 00/08970</b>	International filing date (day/month/year) <b>14/09/2000</b>	(Earliest) Priority Date (day/month/year) <b>23/09/1999</b>
Applicant <b>VANTICO GMBH &amp; CO. KG</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.  
 It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

- the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- contained in the international application in written form.
  - filed together with the international application in computer readable form.
  - furnished subsequently to this Authority in written form.
  - furnished subsequently to this Authority in computer readable form.
  - the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.  Certain claims were found unsearchable (See Box I).

3.  Unity of invention is lacking (see Box II).

## 4. With regard to the title,

- the text is approved as submitted by the applicant.
- the text has been established by this Authority to read as follows:

## 5. With regard to the abstract,

- the text is approved as submitted by the applicant.
- the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

## 6. The figure of the drawings to be published with the abstract is Figure No.

- as suggested by the applicant.
- because the applicant failed to suggest a figure.
- because this figure better characterizes the invention.

None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/08970

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G59/50 C08G59/18

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 280 074 A (KIRTLAND ET AL.) 18 October 1966 (1966-10-18)	1-4,6,7
Y	column 7, lines 4-55 column 8, line 24-44; claims 1,5 ----	5
Y	US 4 195 152 A (FLOYD DON E) 25 March 1980 (1980-03-25) the whole document ----	1-7
Y	US 4 310 695 A (DANTE MARK F) 12 January 1982 (1982-01-12) the whole document ----	1-7
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

7 December 2000

Date of mailing of the international search report

19/12/2000

Name and mailing address of the ISA

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NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Rousseau, F

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/08970

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 199831 Derwent Publications Ltd., London, GB; Class A21, AN 1998-357763 XP002154912 &amp; JP 10 140125 A (NISSAN MOTOR CO LTD), 26 May 1998 (1998-05-26) abstract</p> <p>-----</p>	1-7

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/08970

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
- US 3280074	A 18-10-1966	BE 620967 A FR 1359072 A NL 281529 A		24-07-1964
US 4195152	A 25-03-1980	US 4126640 A BE 869250 A CA 1111070 A DE 2833170 A DK 340678 A FR 2399404 A GB 2002372 A, B IE 47213 B IT 1160567 B JP 54027504 A MX 150941 A NL 7807673 A		21-11-1978 16-11-1978 20-10-1981 15-02-1979 02-02-1979 02-03-1979 21-02-1979 25-01-1984 11-03-1987 01-03-1979 23-08-1984 05-02-1979
US 4310695	A 12-01-1982	NONE		
JP 10140125	A 26-05-1998	NONE		

**XP 002154912**

AN - 1998-357763 [31]

AP - JP19960312572 19961111

CPY - NSMO

DC - A21 A95 Q22

FS - CPI;GMPI

IC - B62D29/04 ; C08G59/50 ; C09J163/00

MC - A05-A01E A08-D03 A08-R03 A10-E18 A11-B09A2 A12-T04D

PA - (NSMO ) NISSAN MOTOR CO LTD

PN - JP10140125 A 19980526 DW199831 C09J163/00 005pp

PR - JP19960312572 19961111

XA - C1998-110257

XIC - B62D-029/04 ; C08G-059/50 ; C09J-163/00

XP - N1998-280195

AB - J10140125 A rigid reinforcer for panels obtd. by laminating an aluminium or stainless steel thin sheet to a sheet material comprises a one pack thermosetting epoxy resin compsn.

- The one pack thermosetting epoxy resin compsn. contains:
  - (1) 100 pts.wt. of an epoxy resin mixt. at a wt. ratio of liq. epoxy resin/solid epoxy resin of 1/9-9/1,
  - (2) 15-35 pts.wt. of a curative obtd. by reacting an epoxy-amine adduct obtd. by reacting an amino cpd. of formula (I) and an epoxy resin at an equiv. ratio of epoxy gp./amino gp. of 1-2/1 and a phenolic cpd.; and
  - (3) 1-10 pts.wt. carbon black.
- (R1)(R2)N-X-NH<sub>2</sub> (I)
- R<sub>1</sub>, R<sub>2</sub> = 1-5C alkyl; and
- X = 1-5C alkylene.
- USE - Used for car body panels.
- ADVANTAGE - The rigid reinforcers have high storage stability and curing properties and can cure and exhibit specific functions on adhering to a panel after electrodeposition coating for avoiding corrosion, if necessary, and baking at a relatively low temp. for intermediate and top coats.
- (Dwg.0/1)

IW - RIGID REINFORCED PANEL CAR BODY PANEL COMPRISE EPOXY RESIN COMPOSITION CONTAIN CURE OBTAIN REACT EPOXY AMINE ADDUCT AMINO COMPOUND CARBON BLACK

IKW - RIGID REINFORCED PANEL CAR BODY PANEL COMPRISE EPOXY RESIN COMPOSITION CONTAIN CURE OBTAIN REACT EPOXY AMINE ADDUCT AMINO COMPOUND CARBON BLACK

NC - 001

OPD - 1996-11-11

ORD - 1998-05-26

PAW - (NSMO ) NISSAN MOTOR CO LTD

Tl - Rigid reinforcers for panels for use in car body panels - comprises epoxy resin composition containing curative obtained by reacting epoxy amine adduct with amino compound, and carbon black

A01 - [001] 018 ; P0464-R D01 D22 D42 F47 ; H0328 ; M9999 M2073 ; L9999 L2391 ; L9999 L2073 ; K9665 ;

- [002] 018 ; R00470 G1161 G1150 G1149 G1092 D01 D11 D10 D19 D18 D32 D50 D76 D93 F32 F30 ; G1570-R G1558 D01 D11 D10 D23 D22 D31 D42 D50

D69 D73 D83 F47 7A ; H0022 H0011 ; P1898-R P0464 D01 D10 D11 D18 D19  
D22 D42 D76 F34 F47 ; H0328 ; M9999 M2073 ; L9999 L2391 ; L9999  
L2073 ; K9665 ; P0475 ;  
- [003] 018 ; K9574 K9483 ; N9999 N5721-R ; N9999 N7192 N7023 ;  
Q9999 Q7818-R ; K9892 ; K9701 K9676 ; B9999 B4079 B3930 B3838 B3747  
; ND01 ; K9552 K9483 ; Q9999 Q9234 Q9212 ; Q9999 Q9289 Q9212 ;  
K9483-R ; K9698 K9676 ; B9999 B4988-R B4977 B4740 ; K9449 ; B9999  
B3532 B3372 ; K9745-R ; B9999 B5243-R B4740 ; B9999 B4148 B4091  
B3838 B3747 ;  
- [004] 018 ; R05085 D00 D09 C- 4A ; A999 A237 ; A999 A102 A077 ;  
- [005] 018 ; A999 A157-R ;  
A02 - [001] 018 ; R00470 G1161 G1150 G1149 G1092 D01 D11 D10 D19 D18 D32  
D50 D76 D93 F32 F30 ; G1570-R G1558 D01 D11 D10 D23 D22 D31 D42 D50  
D69 D73 D83 F47 7A ; H0022 H0011 ; P1898-R P0464 D01 D10 D11 D18 D19  
D22 D42 D76 F34 F47 ; A999 A157-R ; A999 A782 ; L9999 L2391 ;  
L9999 L2039 ; L9999 L2200 ; M9999 M2039 ; M9999 M2200 ; H0226 ;  
P0475 ;  
- [002] 018 ; P0464-R D01 D22 D42 F47 ; A999 A157-R ; A999 A782 ;  
L9999 L2391 ; L9999 L2039 ; L9999 L2200 ; M9999 M2039 ; M9999  
M2200 ; H0226 ;  
- [003] 018 ; B9999 B5629 B5572 ;  
- [004] 018 ; R05139 D01 D11 D10 D50 D87 F09 F07 ; H0226 ;  
A03 - [001] 018 ; P0226 P0282-R D01 D18 F30 ; L9999 L2391 ; L9999 L2200 ;  
M9999 M2200 ; H0226 ; A999 A157-R ; A999 A782 ;  
- [002] 018 ; B9999 B5629 B5572 ;  
- [003] 018 ; H0226 ;  
A04 - [001] 018 ; P0000 ;  
- [002] 018 ; K9574 K9483 ; N9999 N5721-R ; N9999 N7192 N7023 ;  
Q9999 Q7818-R ; K9892 ; K9701 K9676 ; B9999 B4079 B3930 B3838 B3747  
; ND01 ; K9552 K9483 ; Q9999 Q9234 Q9212 ; Q9999 Q9289 Q9212 ;  
Q9999 Q7136 Q7114 ; B9999 B5447 B5414 B5403 B5276 ;

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08G59/50 C08G59/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y		5
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	-/-	

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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

7 December 2000

Date of mailing of the international search report

19/12/2000

Name and mailing address of the ISA

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Authorized officer

Rousseau, F

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 199831 Derwent Publications Ltd., London, GB; Class A21, AN 1998-357763 XP002154912 &amp; JP 10 140125 A (NISSAN MOTOR CO LTD), 26 May 1998 (1998-05-26) abstract</p> <p>-----</p>	1-7

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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US 4195152	A	25-03-1980		US 4126640 A BE 869250 A CA 1111070 A DE 2833170 A DK 340678 A FR 2399404 A GB 2002372 A,B IE 47213 B IT 1160567 B JP 54027504 A MX 150941 A NL 7807673 A		21-11-1978 16-11-1978 20-10-1981 15-02-1979 02-02-1979 02-03-1979 21-02-1979 25-01-1984 11-03-1987 01-03-1979 23-08-1984 05-02-1979
US 4310695	A	12-01-1982		NONE		
JP 10140125	A	26-05-1998		NONE		